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Spin Resonance Studies on Structural Phase Transition in SnTe Crystals+

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X-band spin resonance measurements have been carried out from 1.5 K to 250 K on degenerate magnetic semiconductors $Sn_{1-x}Cr_xTe$ (x=1 at.%) with different carrier concentrations ranging from 2×10^{20} to 5×10^{20} cm^{-3}. The anomalies in the g-value and linewidth serve to identify the structural phase transition temperature T_s. Our results indicate that T_s is independent of the carrier concentration, in contrast to the results found by other workers.

SnTe has been known to undergo a structural phase transition at a well-defined critical temperature T_s. This has been investigated by neutron scattering,[1] Raman scattering,[2] X-ray diffraction,[3] Hall mobility,[4] de Haas-van Alphen effect,[5] electron paramagnetic resonance,[6] and resistivity measurements.[7] In particular, Kobayashi et al. have shown that T_s is dependent on carrier concentration and fitted their experimental results with theoretical curves using the electron-TO phonon interaction model.[7]

In an attempt to verify their conclusion, we have performed spin resonance experiments on $Sn_{1-x}Cr_xTe$ (x=1 at.%) with carrier concentration ranging from 2×10^{20} to 5×10^{20} cm^{-3} over the temperature range 1.5-250 K. $Sn_{1-x}Cr_xTe$ is a ferromagnetic material

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with the Curie temperature $T_c \simeq 297$ K,[8] and thus under the condition of the present experiments at $T < T_c$ we are essentially observing the ferromagnetic resonance (FMR) of the Cr centers. The resonance signals should be a good microscopic probe for identification of the structural phase transition since the g-value as well as the linewidth ΔH are very sensitive to structural changes or crystalline environment. Such changes were successfully observed in our samples of $Sn_{1-x}Cr_xTe$ and they serve to identify the transition temperature T_s.

The Bridgman method was used to grow the crystalline ingots. Cylindrical samples of dimensions 1.8 mmϕ x 4.4 mm were spark-cut from the ingot. The surfaces of these samples were lapped to a mirror-like finish (final lappling powder of 0.3 μm alumina) and then chemically etched. They were annealed at 600°C under Zn vapor for different annealing time to control the carrier concentration.[9] After annealing the samples were again lapped and etched before the measurements. A Varian E-109 EPR spectrometer and a home-made temperature controller capable of maintaining temperatures to within 0.5 K were used. The temperature range was from 1.5 to 250 K.

The resonance signals of Cr centers were found to be independent of the magnetic field direction. Figure 1 shows the temperature dependence of the g-value and the linewidth ΔH for the sample

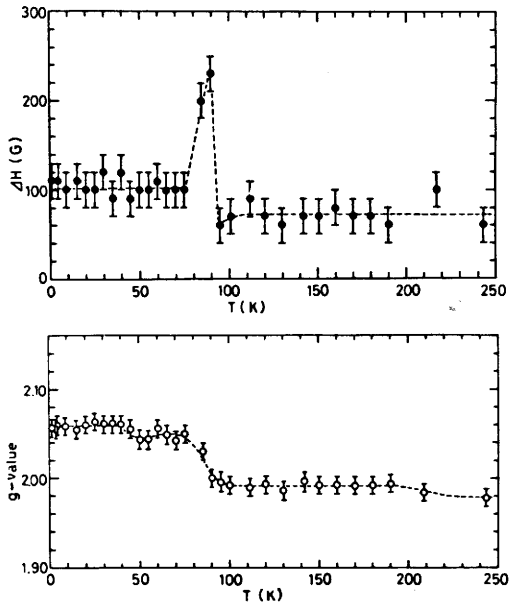

Fig. 1. Temperature dependence of the g-value and the linewidth ΔH for $Sn_{1-x}Cr_xTe$ (x=1 at.%) with $p=2 \times 10^{20}$ cm^{-3}.

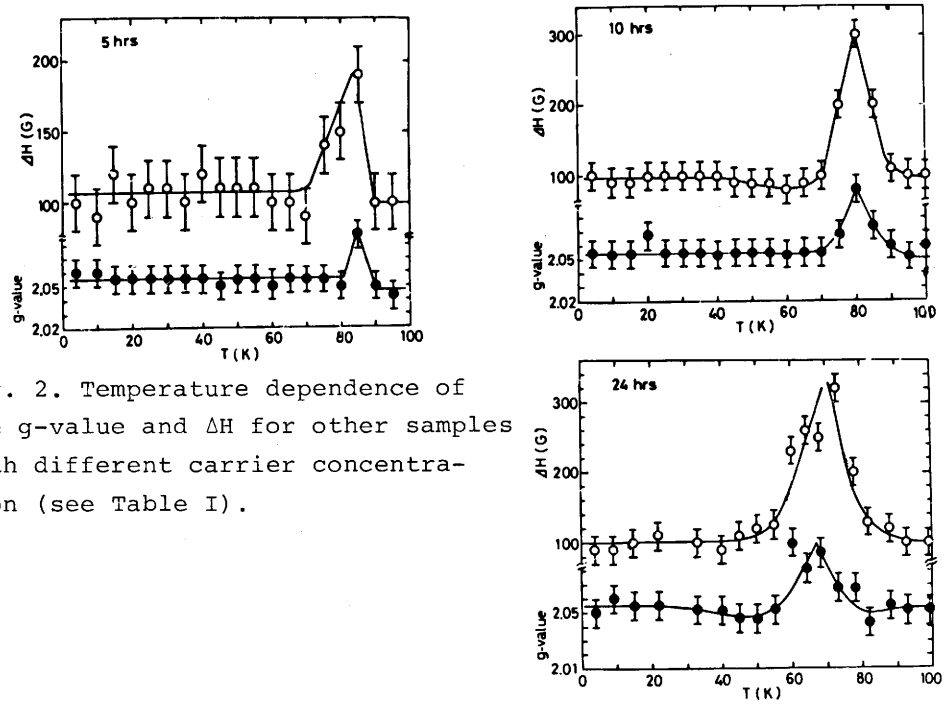

Fig. 2. Temperature dependence of the g-value and ΔH for other samples with different carrier concentration (see Table I).

with the carrier concentration p=2 x 10^{20} cm^{-3}. Similar data for other samples with different carrier concentrations are shown in Fig. 2. It should be noted that these curves show the divergent behaviors in both quantities near 80 K. As is well known, the 3d ions with spin S greater than 1/2 have nondegenerate orbital ground states and large zero field splitting that are sensitive to the strength and the symmetry of the local crystal field. Thus these ions serve as a good probe for identification of the displacive phase transition.[10] Near the phase transition temperature T_s the linewidth usually increases as $(T_s - T)^{-1/2}$ because the fluctuations in the lattices around the ions give rise to the fluctuations in the resonance magnetic field. Also the changes in the linewidth are associated with those in the spin-lattice or spin-spin relaxation time near T_s, since the magnitude of the relaxation time is essentially dependent of the strength of the coupling of the spin system to the crystal lattices. Moreover, through the changes in the effective distance between the ions (and thus exchange interactions) as well as in the crystal symmetry arising from the structural phase transition, the g-value is also expected to change. From these considerations and by comparing the reported values of

T_s,[7] we identify the temperature of about 80 K as the structural phase transition temperature.

All these T_s's are tabulated in Table I, together with the critical region δT_s. It was found that as the carrier concentration p is increased the resonance signals above liquid nitrogen temperatures become weaker and weaker and cannot be detected for samples with $p > 6 \times 10^{20}$ cm^{-3}, and thus we cannot determine T_s for such

Table I. Sample characteristics; annealing time t, nominal carrier concentration p at 77 K,[9] transition temperature T_s, and critical region δT_s.

t (hrs)	p (x 10^{20} cm^{-3})	T_s (K)	δT_s (K)
5	4.5	85	∿20
10	3.5	80	∿20
24	2.5	72	∿20
48	2.0	85	∿20

samples. Figure 3 shows the plot of T_s vs carrier concentration p in which the results of Kobayashi et al. are also drawn for com-

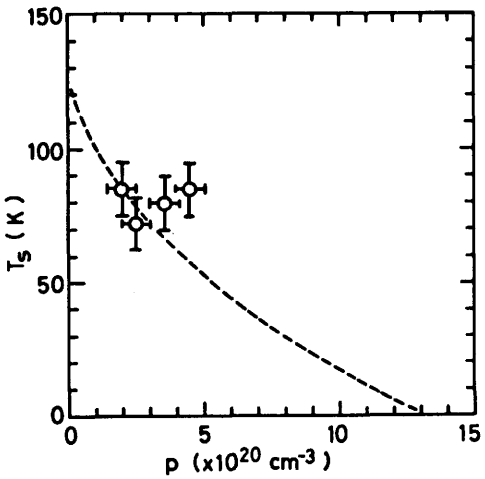

Fig. 3. Structural phase transition temperature T_s vs carrier concentration p. The dotted line is the theoretical curve by Kobayashi et at.[7]

parison. In contrast to their results, our measurements indicate that T_s is independent of p of the host SnTe crystal. At present we cannot give a satisfactory explanation on the difference between the present results and those reported by other workers.[7,11]

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